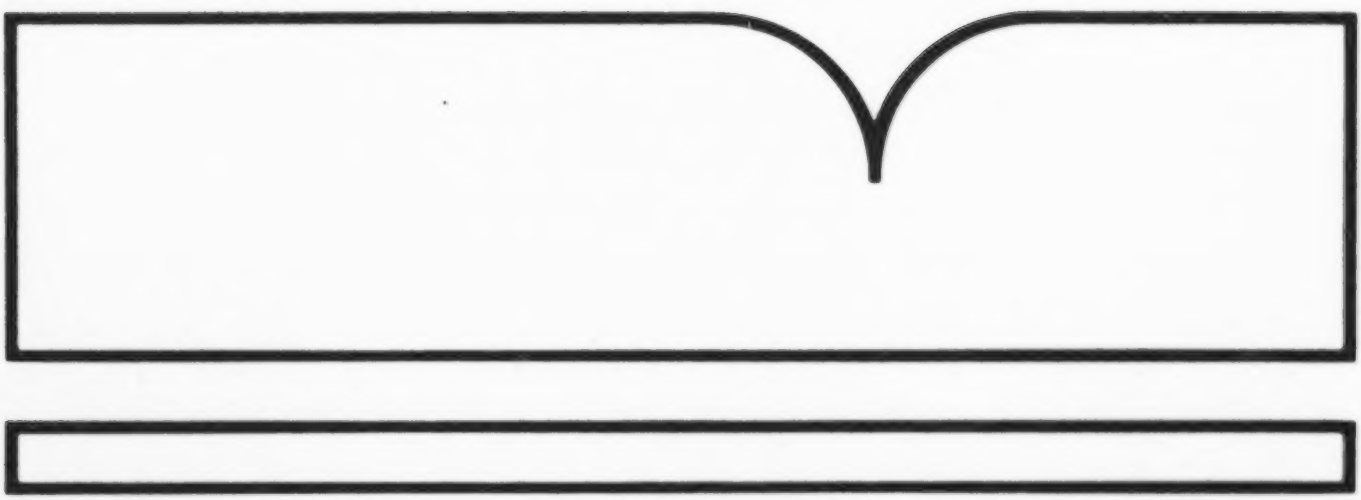
PB87-179743

Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

1987



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RE PB87-179743
EPA/600/J-87/006		

4. TITLE AND SUBTITLE	5. REPORT DATE
On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator: I. Prototype Solid Plastic Wastes (Journal Version)	1987
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. Linak, J. Kilgroe, J. McSorley (EPA/AEERL); J. Wendt (University of Arizona); and J. Dunn (University of Arkansas)	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
See Block 12.	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711	Journal article; May 1986
	14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is William P. Linak, Mail Drop 65, 919/541-5792. Submitted to APCA Journal. Vol. 37, No. 1, pp. 54-65.

16. ABSTRACT The article discusses a statistically designed parametric investigation to determine which waste and kiln variables (charge mass, charge surface area, charge composition, and kiln temperature) significantly affect both instantaneous intensity and total magnitude of the puffs leaving a kiln used to incinerate simple prototype plastic wastes, ranging from polyethylene to polyvinylchloride. Results show the relative ease with which failure conditions are achieved, even at high excess air values and high kiln temperatures. Transient puffs leaving the kiln contain a number of hazardous compounds. Increasing kiln temperature does not necessarily decrease the puff intensity and may in fact cause an increase. However, the total mass emitted always decreases with increasing temperature. In addition, the mass, surface area, and composition of the charge are all important.

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Kilns Simulators Waste Disposal Toxicity Plastics Polyethylene Polyvinylchloride	Pollution Control Stationary Sources Incineration Hazardous Waste Principal Organic Hazardous Constituents	13B 13A 14B 06T 11I

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	13
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

EPA/600/J-87/006
JOURNAL ARTICLE

HAZARDOUS WASTE MANAGEMENT

On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator

I. Prototype Solid Plastic Wastes

William P. Linak, James D. Kilgroe, Joseph A. McSorley

U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Jost O. L. Wendt
Department of Chemical Engineering
University of Arizona
Tucson, Arizona

James E. Dunn
Department of Mathematical Sciences
University of Arkansas
Fayetteville, Arkansas

In the operation of practical rotary kiln incinerators, the hazardous waste charge is often introduced in drums or containers in a batch mode. The ensuing transient condition, caused by the rapid devolatilization of waste materials, can momentarily deplete or displace local levels of excess oxygen in the kiln, resulting in heavy transient loadings of unburned gaseous and particulate hydrocarbons (here denoted as "puffs") leaving the kiln. This system upset must then be handled by an afterburner and subsequent air pollution control devices downstream. Such an overcharging or transient condition may even result in unacceptably low destruction of principal organic hazardous constituents (POHC) and the formation of products of incomplete combustion (PIC).

A 73-kW (250,000-Btu/h) rotary kiln simulator was designed and constructed to provide engineering insight into the chemical and physical parameters associated with failure mode conditions. To this end, a statistically designed parametric investigation was undertaken to determine which waste and kiln variables (charge mass, charge surface area, charge composition, and kiln temperature) significantly affect both instantaneous intensity and total magnitude of the pollutant puffs leaving the kiln. Emphasis was on the incineration of simple prototype plastic wastes, ranging from polyethylene to polyvinyl chloride.

Results demonstrate the relative ease with which failure conditions are experienced, even at high excess air values and high kiln temperatures. Transient puffs leaving the kiln contain a number of hazardous compounds. Increasing kiln temperature does not necessarily decrease the puff intensity and may in fact cause an increase. However, the total mass emitted decreases with increasing temperature. In addition, the mass, surface area, and composition of the charge are all important.

In recent years the issue of hazardous waste management has been of growing concern to the public, industrial, and government sectors. Thermal destruction or incineration is usually thought to be a safe and efficient means of destroying a wide variety of organic materials, but potential problems encompassing the diverse combustion characteristics of organic wastes, the incomplete destruction and removal efficiencies (DRE) of the principal organic hazardous constituents (POHC), the formation of secondary pollutants or products of incomplete combustion (PIC), and the fate of metal and other inorganic constituents during the combustion process make this technology more complex than it might appear.

Of the approximately 340 incinerators that have come into service in the U.S. since 1969, 12.3 percent are of the rotary kiln design.[1] Rotary kiln incinerators may comprise one of the most versatile and most universal waste disposal systems available.[2] Gaseous and pumpable wastes can be charged through standard burners into the kiln. Solid material and liquid filled drums or containers can be fed through entrance chutes, typically cocurrent with the gas flow. The kiln rotation continuously exposes fresh surfaces for oxidation and provides for constant ash removal. Kiln angle and rotation speed determine the solids residence time and ensure complete burnout of steel drums and inorganic residues. These materials are usually water quenched and removed by conveyor for landfill. A secondary combustion chamber (afterburner) is usually provided for further destruction of unburned gaseous and suspended particulate organics. Together, the rotary kiln and afterburner accomplish the task of providing turbulent mixing of the waste species with excess oxygen at high temperatures and at residence times sufficient to destroy the organic waste to within tolerable levels. Combustion gases are then quenched and scrubbed of acid and particulates before discharge to the environment.

Copyright 1987–APCA

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

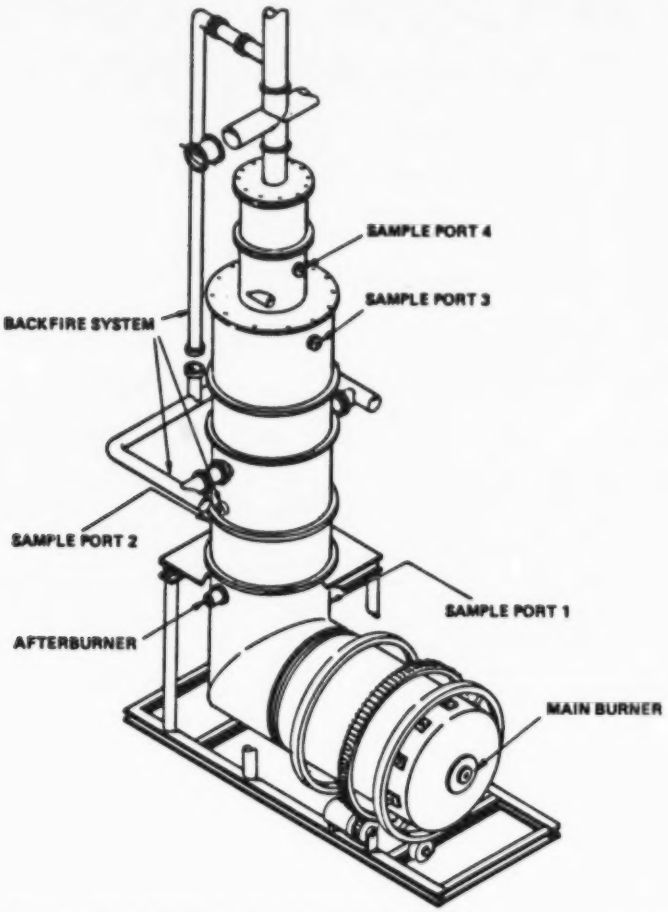


Figure 1. EPA incinerator simulator, 3-dimensional view.

Rotary kiln incineration systems have been described elsewhere[3,4] and have been shown to be generally safe and effective under steady-state operation.[5,6] Although data exist on the DREs of many hazardous and surrogate waste materials under steady-state rotary kiln operating conditions,[6,7] little information is available on potential problems under the transient conditions that occur when drummed or solid materials are batch-fed into the combustion chamber. In typical practice, drums are charged at a rate of six to 12 per hour. A possible transient condition relates to overcharging of the kiln, which can occur if waste parameters are not properly matched to the incinerator operating conditions and can lead to heavy transient loads on the afterburner and downstream gas clean-up systems.

Overcharging is a transient phenomenon which occurs when a charge of waste material entering the incinerator momentarily overloads the ability of the incinerator to destroy the waste. As a transient problem, its investigation requires the real-time measurement of undestroyed species exiting from the kiln or afterburner sections. Overcharging, however, may not only result in the poor destruction of the POHCs, but may also result in the formation of large quantities of PICs. In fact, it may be possible to adequately destroy the POHCs and still produce substantial amounts of PICs, which may be of equal or greater environmental concern.

The overall objective of the research described in this paper is to identify potential problem areas of rotary kiln incineration, with the goal of developing predictive methods that correlate transient incinerator performance and possible failure modes with waste characteristics, kiln operating parameters, and continuous on-line instrumentation. A first step is to gain engineering insight and understanding into the combustion phenomena occurring in the kiln itself, rather than to evaluate the field performance of an actual incinerator/afterburner/scrubber system taken as a whole. To this end, a laboratory-scale rotary kiln simulator has been designed and fabricated. Its purpose is to conduct parametric studies on factors that influence the occurrence of transient puffs of surrogate wastes introduced in a batch mode. This research, therefore, does not focus primarily on DREs of specific POHCs nor does it evaluate any specific rotary kiln incinerator design. Rather, it attempts to delineate, in a generic sense, what fundamental combustion phenomena are important and worthy of further study and why. The value in utilizing a prototype rotary kiln simulator, rather than an actual permitted field device, lies in its ability to allow parametric variation in a controlled fashion without loss of the overall complicated salient features of practical kiln operation. In this way, it is possible to adopt a research approach in which hypotheses are formulated and proven or disproven. Throughout this paper we use the term "puff" to describe any measurable transient condition caused by the devolatilization and combustion of batch-fed waste material. While in many instances these system upsets resulted in incomplete combustion and dark exhaust plumes, the definition of a "puff" is not limited exclusively to these failure mode conditions.

This paper consists of four parts. First the rotary kiln simulator utilized is described in detail. Then its performance characteristics are compared to those of full-scale units to validate the facility as a useful laboratory prototype of a rotary kiln incineration process. The third part of this paper describes experimental results of parametric studies delineating the occurrence of transient puffs resulting from the batch introduction of prototype solid plastic wastes into the kiln. A statistically designed experiment allowed determination of the individual effects of charge mass, charge surface area, plastic type, and kiln temperature on both the total integrated amount and the instantaneous magnitude of volatile hydrocarbons exiting the kiln. In order to establish the relationship between these measurements and potential POHC destruction and PIC formation problems, detailed analytical measurements of semivolatile, moderate molecular weight organic species are then described in the fourth part of this paper. These semivolatile species, together with the fully and partially oxidized combustion gases, volatile hydrocarbons, heavy organics, and particulates, constitute the puff. In all cases, measurements were made of combustion products leaving the kiln itself, prior to subsequent destruction by an after-

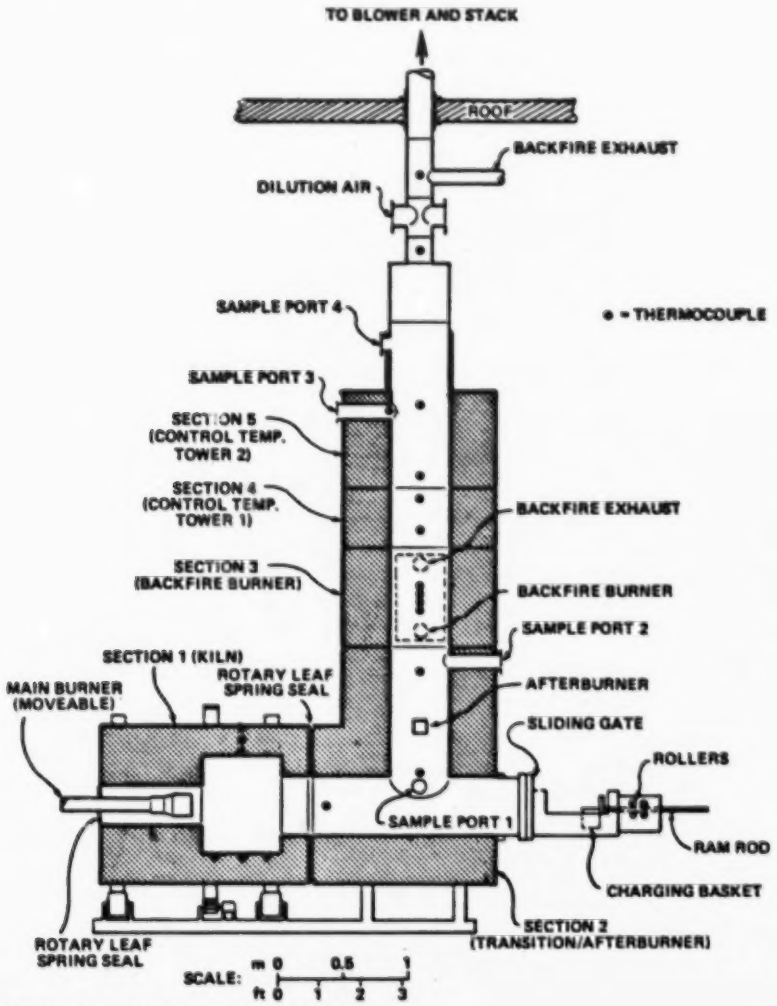


Figure 2. EPA incinerator simulator, cutaway view.

burner or removal by a scrubber. The conclusions drawn relate, therefore, to the performance of the kiln only, not to that of a rotary kiln/afterburner/scrubber system. The results allow us to determine the inlet transient conditions with which an afterburner must be capable of dealing, and how these depend on kiln and solid waste parameters.

Rotary Kiln Simulator

A 73 kW (250,000 Btu/h) prototype rotary kiln thermal destruction unit was designed for the testing of solid surrogate hazardous waste materials and is shown in Figures 1 and 2. It was designed to contain the salient features of practical kilns, but still be sufficiently versatile to allow parametric experimentation by varying one parameter at a time or controlling a set of parameters independently. The simulator consists of five steel-shelled, refractory-lined sections (kiln, transition/afterburner, backfire burner, control temperature tower 1, and control temperature tower 2, as shown in Figure 2. Internal radial dimensions vary from 0.762 m (30 in.) in the kiln recess to 0.457 m (18 in.) in the transition and tower sections. Outside diameters vary from 1.168 to 1.219 m (46 to 48 in.). Internal axial dimensions total approximately 6.096 m (240 in.) from the front burner wall to the point of dilution air addition. The rotating kiln section contains a 0.610 m (24 in.) recess in which the solid waste is contained during incineration. The recess area was designed with a length to diameter (L/D) ratio of 0.8, which is 20–25 percent of a full-scale system. In reality, the kiln is considered to extend to the centerline of the tower sections, 1.727 m (68 in.) from the front burner wall, containing both rotating and stationary parts and yielding a L/D ratio of approximately 3.8. Further details regarding the scaling of the simulator with respect to full-scale units are presented in a later section.

The main burner (Eclipse 82 MVTA) is the primary heat source to the system. It is positioned to fire into the kiln as shown in Figure 2. The kiln rests on two trunion assemblies and is driven by a motor and gear drive. Consistent rotational speeds between 0.1 and 3.0 rpm are possible. Seals between the kiln and the transition/afterburner section and main burner extension are made with Teflon gasketed rotary leaf springs. Table I summarizes the design characteristics of the Environmental Protection Agency (EPA) rotary kiln simulator.

From the kiln, the combustion products enter the transition/afterburner section. The afterburner (Eclipse 51.5 MVTA) provides heat and flame to this secondary combustion chamber. The backfire burner and control temperature tower sections are designed to allow operation of the secondary combustion chamber at adjustable and controllable temperatures. The two backfire burners (180 degrees opposed) burn natural gas in an annular section between layers of refractory. By this means, additional and variable heat can be imparted to the kiln gases without dilution by additional combustion products. The design permits a wide variety of time/temperature profiles to be achieved in the control temperature sections. However, for all the results reported in this paper, these features were never utilized, and there was neither supplemental heating nor afterburning downstream of the kiln exit. In this way, the kiln could be isolated and the characteristics of primary incineration could be examined alone.

Sampling and Analysis

Four sampling ports located along the axis of the simulator allow for the extractive sampling of combustion products. Continuous monitors measure concentrations of combustion gases—O_2 (Beckman model 755 paramagnetic); CO, CO_2 (Beckman model 654 infrared); NO_x (Thermo Electron model 10A chemiluminescent); and total volatile hydrocarbons as methane (Beckman model 402 flame ionization detection). In addition, samples can be directed to a Hewlett Packard model 5840A gas chromatograph or collected for detailed analysis using standard-

ized methods with VOST (volatile organic sampling train) and SASS (source assessment sampling system) techniques.[8,9] A heated sample line (420 K, 300°F) is used to transfer the total volatile hydrocarbon sample. Twenty-four unshielded type K thermocouples allow for process temperature measurement and control. Thermocouples are positioned along the length of the simulator extending into the combustion zones and imbedded at various depths in the refractory. Positions of the sampling ports and thermocouples are illustrated in Figure 2.

Surrogate waste materials are batch charged through a sliding gate/ram assembly located on the transition/afterburner section (Figure 2). After solids or contained liquids are placed in the charging basket, the gate is opened and the basket is rammed into the kiln. At a mechanically set stop position, the basket is stopped and the momentum carries the charge into the kiln recess. The basket is then withdrawn and the gate closed. A cover placed over the charging assembly minimizes air infiltration into the kiln. The entire charging operation typically takes less than 4 seconds.

Quantification of a system upset condition requires the real-time measurement of system variables. Peak responses of combustion gas and hydrocarbon analyzers yield an indication of extremes. Other useful variables, however, are the time-integrated responses and, in particular, the time-integrated response of the total volatile hydrocarbon analyzer. Through this method an indication of emitted mass can be determined. By holding constant sampling temperatures, pressures, and flow rates, consistent volumetric flow is delivered to the analyzer's flame ionization detector (FID). Provided the incinerator flue gas rate is constant, the integrated mass measured is then proportional to the total mass of volatile hydrocarbons passing up the stack during a puff. The peak response, on the other hand, represents the maximum concentration in a puff.

Simulator Performance and Facility Validation

Table I presents a comparison between the operating characteristics of the EPA simulator and those of full-scale rotary kiln incinerators.[1,5] The simulator matches the volumetric heat release and the gas phase residence times of full-scale units, but is rated at less than 5 percent of the gross heat input of full-scale units.

Figure 3 shows the axial time/tem-

Table I. Rotary kiln characteristics, full-scale vs EPA simulator.

	Full-scale	EPA simulator
Heat input, kW (Btu/h)		
Mean	10431 (35.6E + 06)	73 (0.25E + 06)
Median	3018 (10.3E + 06)	
Heat release, kW/m³ (Btu/h ft³)	155–414 (15,000–40,000)	259 (25,000)
Kiln exit temperature, K (°F)		
Range	533–1533 (500–2300)	1089–1366 (1500–2000)
Typical value	922–1144 (1200–1600)	
Afterburner exit temperature, K (°F)		
Range	1144–1811 (1600–2800)	1366–1477 (2000–2200)[a]
Typical value	1366–1589 (2000–2400)	
Kiln residence time		
Solids, h	<2	N/A
Gases, sec	1–3	2–3
Afterburner residence time, sec		
Range	1–4	3–4[a]
Typical value	2	
Excess air, percent		
Range	75–210 (SR = 1.75–3.10)	10–200 (SR = 1.10–3.00)
Rotational speed, rpm	0.25–1.5	0.1–3.0
Peripheral speed, m/min (ft/min)	0.305–1.524 (1–5) (outer surface)	0.244–7.010 (0.8–23) (inner surface)
Length to diameter ratio		
Range	2–10	0.8 (recess)
Typical value	3–4	3.8 (overall)
Angle to horizontal, percent	<2–3	0 (no rake)
Auxiliary fuel, kg/hr (lb/h)	Natural gas or fuel oil (none typically used)	Natural gas 5.22 (11.5) (always used)
Feed capacity		
Solids, kg/h (lb/h)	600–2000 (1320–4410)	
Liquids, l/h (gal./h)	630–2250 (165–590)	

[a] Data presented do not include the use of the afterburner system.

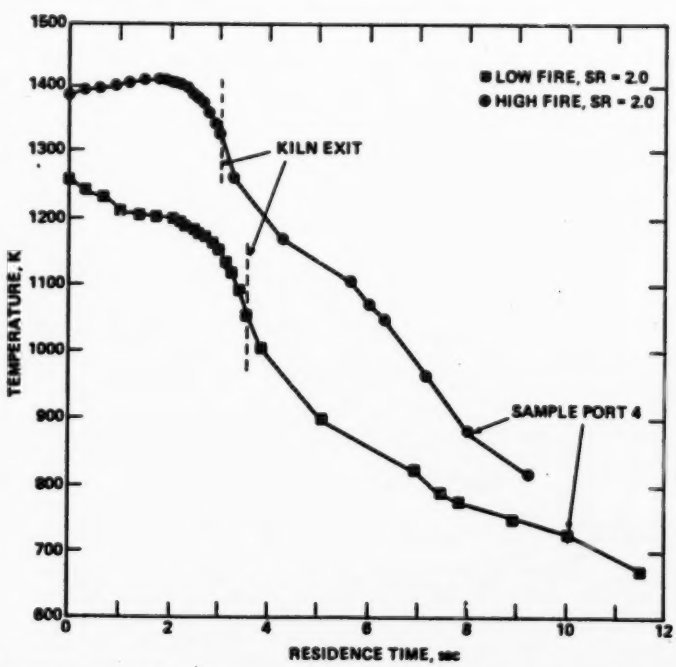


Figure 3. Temperature profile vs residence time, low and high fire test conditions.

Table II. Test matrix design for solid plastic rods.[a,b]

Trial	Surface area	Temperature	Mass	Composition
The first 16 trials test for linear relationships.				
1	1	−1	−1	1
2	−1	1	−1	1
3	−1	−1	1	1
4	1	1	1	1
5	−1	−1	−1	2
6	1	1	−1	2
7	1	−1	1	2
8	−1	1	1	2
9	−1	−1	1	3
10	1	1	1	3
11	1	−1	−1 (0)[c]	3
12	−1	1	−1	3
13	1	−1	1	4
14	−1	1	1	4
15	−1	−1	−1	4
16	1	1	−1	4
The next 8 trials test for curvilinear (quadratic) trends.				
17	0	1	−1	1
18[d]	0	−1	1	1
19	1	0	1 (0)[c]	2
20	−1	0	−1	2
21[d]	1	1	0	3
22	−1	−1	0	3
23	−1	1	1	4
24	1	−1	−1	4

[a] Key: 1 = low density polyethylene (LDPE); 2 = polyvinyl chloride (PVC); 3 = high density polyethylene (HDPE); 4 = polystyrene (PS).
[b] Additional trials (totaling 37) were performed using LDPE.
[c] Substituted trials.
[d] Omitted trials.

moved. In this way, the distance between a charge and the heat release zone can be increased (simulating co-current flow) or decreased (simulating counter-current flow), and the overall residence time of the solid charge is determined by the length of the batch experiment. Thus, the kiln L/D ratio, which together with slope and rotation speed, normally determines the solids residence time in a practical kiln,[2] is not important for this purpose as far as the simulator is concerned. Of critical interest in the determination of transient puff generation is the contacting between the waste or waste products and the main combustion flue gas. It might be argued that the presence of the cavity might exacerbate a poor mixing problem and thus artificially yield puffs, where none might exist in the field. To test whether improved contacting decreases the magnitude of transient puffs, experiments were conducted in which the rotation speed was changed from 0 to 3 rpm. These tests conclusively showed that improved contacting, achieved by increasing rotation speed, yielded larger puffs. Therefore, our tests, in which rotation speed was 1 rpm, yield conservative results, and the generation of the puff in the simulator is not an artifact due to the poor contacting and the presence of the cavity.

perature profile through the kiln and the subsequent control temperature tower (without additional heat input) under the low and high firing conditions utilized in the parametric experiments reported in a later section. Measurements in the kiln were taken with a suction pyrometer with a type R thermocouple. Gas phase temperatures range from 1258 K (1804°F) to 1056 K (1440°F) after 3.6 seconds at the kiln exit and from 1383 K (2030°F) to 1327 K (1928°F) after 3.1 seconds under low and high firing conditions, respectively. These gaseous time/temperature profiles closely simulate full-scale units.

An apparent discrepancy between the simulator design and that of full-scale systems lies in the presence of the cavity in the simulator (not present in full-scale units), and in the resulting apparent discrepancy in L/D ratio (Table I). However, this discrepancy is more apparent than real for the following reasons: First, the simulator does not attempt to reproduce the actual continuous travel of solids along the kiln bottom, but rather simulates this by using a control volume approach in which the solids reside in the cavity and the burner can be continuously

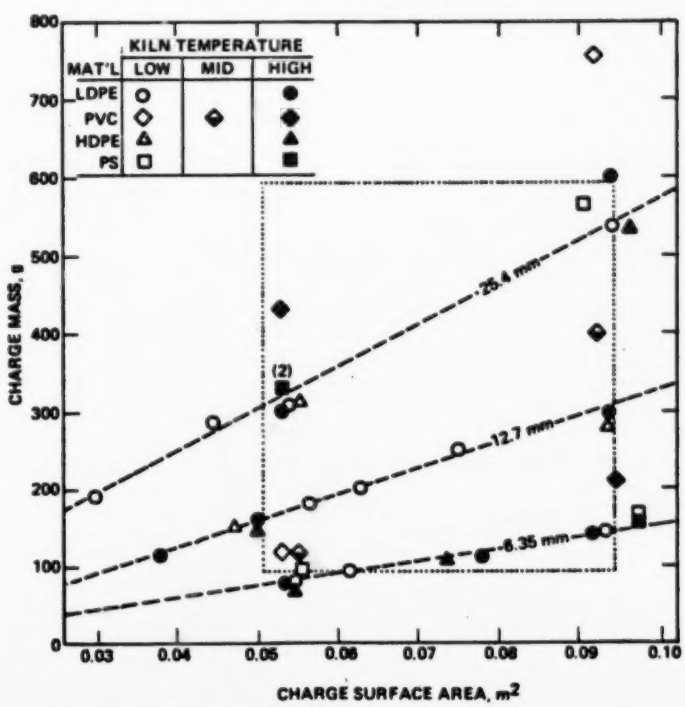


Figure 4. Test conditions for solid plastic rods. Dashed lines define domain accessible to LDPE rods of specified diameters. Dotted lines define boundaries of response surface plots. Each trial consisted of 5 to 10 replicate tests. Duplicate trials denoted by (2).

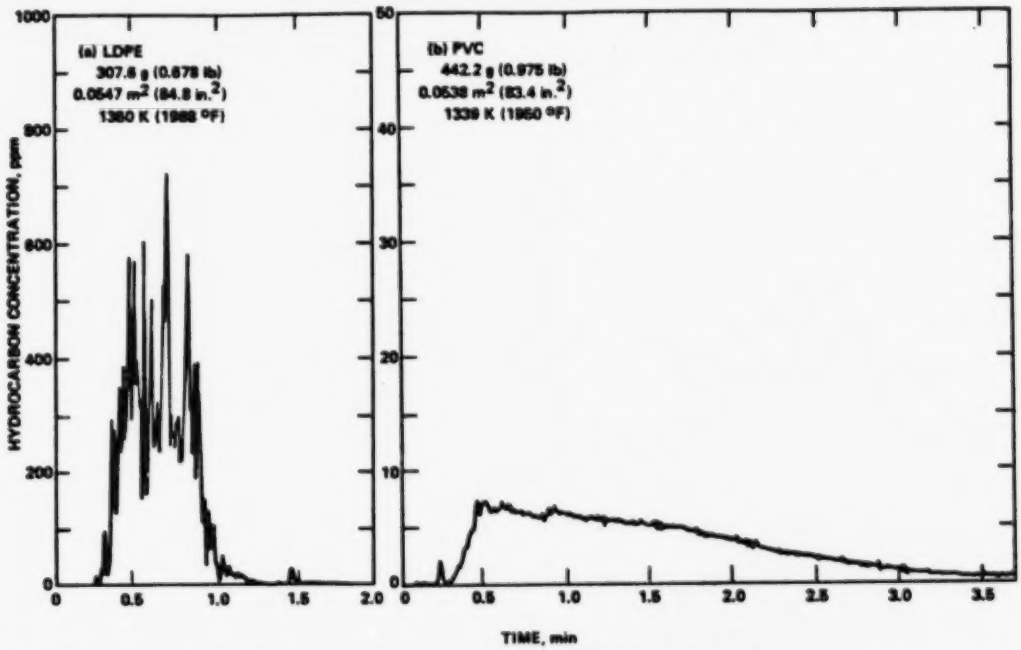


Figure 5. Comparison of LDPE and PVC transient hydrocarbon peak shapes at similar trial conditions.

Preliminary Tests

Preliminary tests were conducted during the shakedown of the rotary kiln simulator to examine the operating parameters that would promote emission failure mode conditions during the incineration of solid waste materials. Wide-mouth polyethylene (PE) 1-gal bottles were chosen to simulate a typical solid waste container since this type of plastic container is actually used in the disposal of solid laboratory wastes that are burned in EPA's commercial incinerator located at the Environmental Research Center, Research Triangle Park, North Carolina. The 1-gal PE bottles weigh approximately 165 g when empty and resemble 1-gal plastic milk bottles. The first test burn consisted of charging one of the empty PE bottles into the rotary kiln simulator. Peak temperature in the kiln was approximately 1644 K (2500°F) and it was rotating at 1 rpm. The main burner was operating at 9.90 m^3/h (350 cfh) of natural gas and 107.6 m^3/h (3800 cfh) of air which represented typical high fire, low excess air conditions (SR = 1.1). The single plastic bottle immediately burst into flame as it dropped into the recess area of the kiln. The continuous on-line emission monitors recorded the levels of O_2, CO, CO_2, NO_x, and total volatile hydrocarbons (THC). A black puff was observed exiting the stack approximately 9 seconds after the plastic bottle was charged into the kiln. The duration of the puff was approximately 45 seconds. Volatile hydrocarbon concentrations in excess of 20,000 ppm (as methane) were measured by the THC analyzer. It was observed that the plastic bottle instantaneously ignited, consuming all of the available local oxygen in the kiln recess. This resulted in flash pyrolysis and a puff which was transported through the system under plug-flow conditions, as evidenced by a very rapid response of the FID.

Replicate tests were carried out to observe the reproducibility and ignition characteristics and to examine the duration of the failure mode transient. The replicate tests proved that the observed puffs occurred between 8 and 10 seconds after charging each bottle (accountable by system and sample line residence times) and the duration of the transient was 45–50 seconds at the same temperature and air-to-fuel firing conditions.

The overall conclusions to be drawn from this section of the paper are (a) transient puffs due to overcharging were easily generated in the rotary kiln simulator and (b) the laboratory kiln closely simulated the overall gas phase times and temperatures and other complicated salient features of full-scale units.

Parametric Studies on Incineration of Plastic Rods

The preliminary screening experiments described above allowed us to formulate the hypothesis that, for a given solid waste compound, the occurrence and magnitude of a transient puff, due to overcharging, depended on charge mass, charge surface area, and kiln temperature. It was also hypothesized that waste composition was important. As prototype solid wastes, we chose solid plastic rods composed of low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), and polyvinylchloride (PVC). These rods were easily obtainable and had well-defined initial shapes. Within a certain mass range, surface area could be changed independently by using various lengths of rods of 6.35 mm (0.25 in.), 12.7 mm (0.5 in.) and 25.4 mm (1.0 in.) diameters. The plastic compounds chosen span a range of molecular structures, molecular weights, and elemental compositions that are of intrinsic interest to the incineration community because they are widely used and disposed of.

The representative kiln temperature used as a control parameter was that measured by a bare type K thermocouple at the kiln exit, 0.965 m (38 in.) from the front burner wall. Low and high fire conditions were used and cor-

respond to the two temperature distributions in Figure 3. The following kiln operating parameters were kept constant for all runs reported here:

(a) Auxiliary gas flow rate, 5.66 m^3/h (200 cfh).
(b) Air flow rate, 109.0 m^3/h (3850 cfh) (leading to constant stoichiometric ratio of 2.0 or excess air of 100 percent).
(c) Rotation speed, 1 rpm.
(d) Burner position, −0.34 m (−13.5 in.) inside the front burner wall.
(e) Kiln pressure, −37.4 Pa (−0.15 in. H_2O).
(f) Sample port, at position 4 (Figure 2).

The above gas and air flow rates correspond to low fire conditions. High fire conditions were achieved by utilizing the thermal capacity of the kiln refractory to store heat and maintain temperature. Steady-state high temperatures were achieved at high gas, low excess air (SR = 1.1) rates. Before each test the gas flow rate was reduced to standard conditions (SR = 2.0) and the kiln temperature was allowed to equilibrate to a pseudo-steady-state value before the waste was charged. This temperature cycling before each test allowed 100 percent excess air (SR = 2.0), natural gas and air flow rates, and other kiln parameters to remain constant for both temperature conditions. Kiln exit gas temperatures varied from 1105 K (1530°F) to 1339 K (1950°F) at low and high fire conditions, respectively.

Statistical Design of Experiments

The general methodology employed in this research was that of response surface experimentation.[10] This methodology allows one to determine, on the basis of one experiment involving a minimal number of trials, an empirical relationship between the response and the controlled parameters in the experimental region. Denoting low, intermediate, and high settings of the three variables (charge mass, charge surface area, and kiln temperature) by −1, 0, and 1, respectively, we formulated the test matrix shown as Table II. Actual minimum and maximum values were determined in part by compatibility with existing instrumentation. The first 16 tests were sufficient to determine linear relationships relating the response to the parameters varied. The additional eight tests allow a quadratic model to be formulated as well as full degree of freedom tests of significance of all main effects and all two-factor interactions.[10]

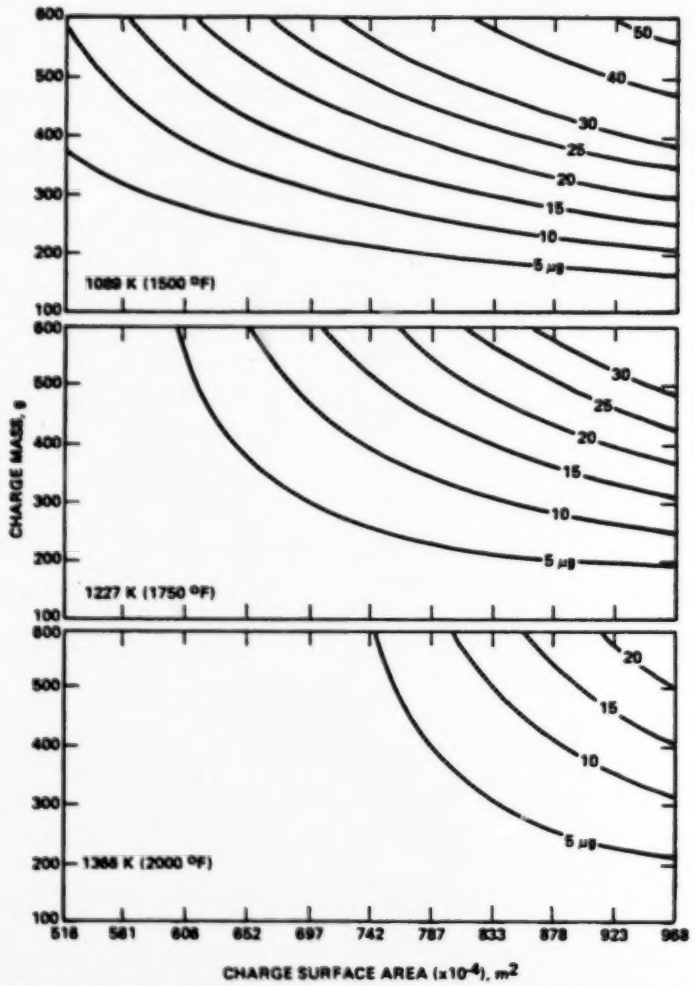


Figure 6. Effect of charge mass, charge surface area, and kiln temperature on integrated LDPE peak area. Contour values denote total hydrocarbons measured as micrograms of methane.

During execution, shortage of some materials forced minor modifications of this matrix. For example, trials No. 18 and 21 were deleted, and the −1 values for charge mass in trials No. 11 and 19 were replaced by 0. However, this was more than compensated for by additional tests on other materials, and the final summary of tests completed is shown in Figure 4. The dashed straight lines define the experimental domain accessible using LDPE rods of specified diameters. Similar straight lines could be drawn for rods of other plastics, but slopes would differ because of different densities. It should be noted that, although charge mass and charge surface area are in general not independent, it was, within a restricted domain, possible to vary charge surface area for a given charge mass by changing rod diameter alone. While Figure 4 includes all test points examined (37 total), the actual test matrix (corresponding to −1, 0, 1) is confined to a smaller area approximately defined by the region within the dotted lines. In actuality, the test matrix was defined by the masses of 6.35, 12.7, or 25.4 mm (0.25, 0.5, or 1.0 in.) diameter plastic rods that yield charge surface areas of approximately 0.0548 m^2 (85 $in.^2$) and 0.0935 m^2 (145 $in.^2$). These masses varied from 80 g (0.176 lb) to 775 g (1.709 lb). It should be noted that the response surface plots (to be presented in a later section) correspond to this reduced area of the total matrix.

Experimental Procedure

The charge, consisting of a variable number of rods 0.15 m (6 in.) in length, was evenly distributed in the charging

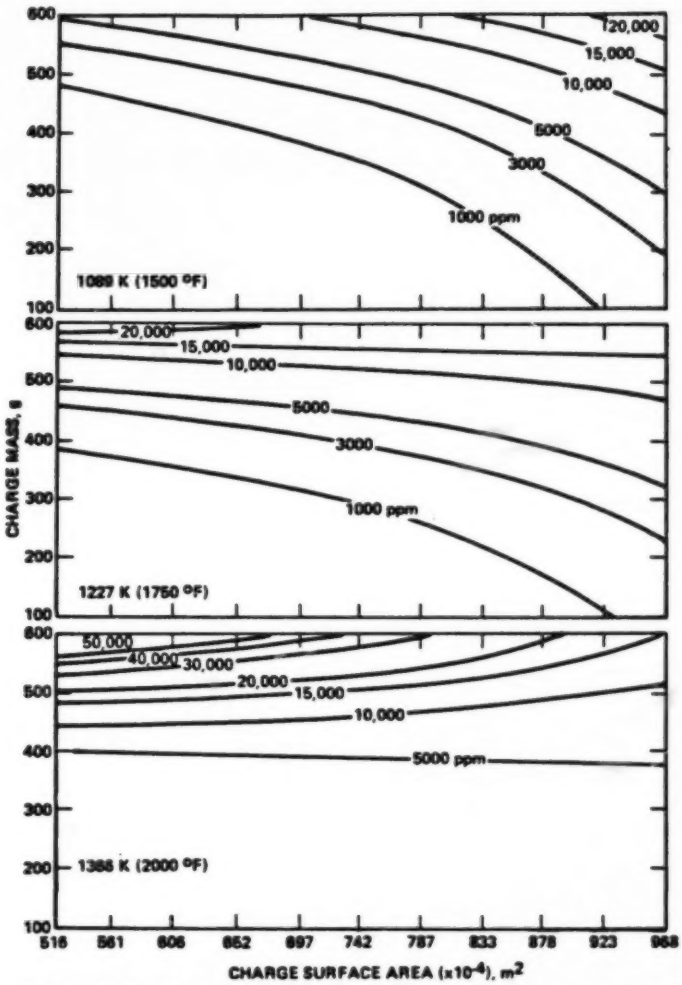


Figure 7. Effect of charge mass, charge surface area, and kiln temperature on absolute LDPE peak height. Contour values denote peak hydrocarbons measured as parts per million of methane.

basket. After all instruments indicated a steady-state baseline condition, the waste was charged. The transient signals from all the instrumental analyzers were recorded, and that from the THC FID integrated. Figure 5 presents typical traces for two different wastes at similar test conditions. Clearly there are significant quantitative and qualitative variations in the mechanisms generating transient puffs from solid wastes of differing compositions. As might be expected from experimentation on equipment of this complexity, there was significant variation in results from replicate tests. However, precision of the averaged peak area response increases roughly as the square root of the number being averaged. Therefore, the number of replicates for each trial ranged typically between 5 and 10 charges, depending on availability of material. The raw data were electronically recorded for subsequent statistical manipulation.

Statistical Analysis of Data

Replicated values of peak area and peak height were averaged. A quadratic response surface model was fitted to the mean values using weighted least squares with the weights equal to the number of replicates. The quadratic model included linear and quadratic dependences on each variable, as well as all the cross-product terms denoting interactions between pairs of variables. The preprogrammed procedures in SAS (Statistical Analysis System) which are relevant to response surface methodology were used to further interpret the data. Similarities in model coefficients between different wastes were statistically tested for evidence that dependences of the response on various parameters differed from waste to waste. Further tests denoted which linear, quadratic, or interaction dependences were statistically significant.

Results: Transient Peak Area

The area under the transient curve measured by the FID is, under the constant sampling conditions described above, proportional to the total quantity of volatile hydrocarbon contained in a puff. Statistical analysis yielded the following final model relating controlled variables to the response:

$$\text{Peak area response } (\mu g\ CH_4) = k_1 + a \cdot T + b \cdot M + c \cdot S \cdot M + d \cdot S \cdot T + e \cdot M \cdot T \quad (1)$$

where M, S, and T are charge mass, charge surface area, and kiln exit temperature, respectively. This model allowed 95.9 percent of the variation among the 37 means (36 independent conditions and one duplicate) to be accounted for by the variation of these predictor variables.

Note that the analysis showed that the linear term in charge surface area, S, was insignificant, but that charge surface area was important through its interactions with charge mass, M, (the $S \cdot M$ term) and kiln temperature, T, (the $S \cdot T$ term). The effects of quadratic terms in M, S, and T were statistically insignificant, in the experimental range covered here. Note also the presence of a significant charge mass by kiln temperature interaction (the $M \cdot T$ term).

The linear coefficient for mass, b, was statistically shown not to vary from waste to waste, possibly indicating that the direct dependence of the puff size on charge mass keeping everything else constant was independent of waste type. By contrast, the dependences of the response on all other parameters did vary quantitatively and qualitatively with waste type. For example, the coefficients a and c were positive for LDPE and HDPE but negative for PVC and PS. The converse was true for d, and e was negative but different for each waste. Changes in the signs of several of these coefficients indicate qualitative differences in the behavior of the various surrogate wastes. The fact that different coefficients were positive for one set and negative for another may indicate the degree of correlation between the wastes of these sets. Certainly, the behavior of the LDPE and HDPE wastes was highly correlated. Additionally, the PVC and PS wastes behaved differently with respect to the

PE wastes and, in many ways, correlated highly with each other. The qualitative dependence of the response on charge mass, M, is best examined by evaluating the experimental range of the quantity $(b + c \cdot S + e \cdot T)$, while that on charge surface area, S, is determined by evaluating the sign and magnitude of $(c \cdot M + d \cdot T)$, and on kiln temperature by evaluating $(a + d \cdot S + e \cdot M)$. These results are best described pictorially through response surface plots, as shown in Figure 6 for the LDPE rods. The magnitude of the contours are in micrograms of hydrocarbons, measured as methane, and they proportionately represent the total amount of volatile hydrocarbons escaping in the puff. The analogous contour plots for HDPE were similar, but those for the PS and PVC contained some similarities but also some significant differences. We focus here solely on the LDPE results because data for that waste were far more numerous than those for the other wastes (Figure 4), and therefore inspire more confidence in the conclusions to be drawn. However, it is important to note that the significant qualitative differences in FID traces between wastes were noticeable in the raw data even before statistical analyses were performed (Figure 5).

Figure 6 illustrates that, for the LDPE, the largest puffs (mass basis) are produced at high charge surface areas and high charge masses; i.e., the contours peak at the top right-hand corner. Furthermore, there exists a threshold charge mass above which puffs rapidly appear, and this threshold is not very sensitive to kiln temperature. An analogous charge surface area threshold also comes into play, but only at the higher kiln temperatures. Therefore, charge surface area is important and, within a certain charge mass range, can also determine the presence and magnitude of a puff. In general, increasing kiln temperature decreases the total amount of volatile hydrocarbon species contained in a puff, which is a significant result. For all wastes examined, increasing the kiln temperature decreased the area under the volatile hydrocarbon trace. Integrated traces for the PS and PVC wastes showed much less effect of surface area than did the LDPE and HDPE wastes. It should be noted that, while the contour plots presented are unique to the data collected, the models presented here for peak area and in the next section for peak height are the "best fit" models. Other "close" models, which account for somewhat less of the total variance, do exist. It is for this reason that undue emphasis should not be placed on the estimated coefficients of these particular models.

Results: Transient Peak Height

Statistical analysis on responses as determined by peak height (in contrast to peak area) yielded, for each waste, an expression of the form:

$$\ln(\text{Peak height response} + 1)\ (\text{ppm } CH_4) = k_2 + v \cdot S + w \cdot T + x \cdot M + y \cdot S \cdot T + z \cdot S \cdot M \quad (2)$$

This model accounts for 84.3 percent of the variability of the 37 averaged data points used. It is significantly different in form from the model for peak area discussed above, and indicates the importance of distinguishing between total mass of the puff and the peak transient concentration of hydrocarbons in the puff. The coefficients v (for charge surface area), y (for the interaction term, $S \cdot T$), and $z(S \cdot M)$ were statistically shown not to differ significantly from waste to waste. Coefficients v, w, and x were positive for all wastes, while y and z were negative.

The resulting contour plots are shown in Figure 7, again for LDPE. The most significant conclusion to be drawn from these contour plots is that, for this waste, increasing the kiln temperature *increased* the maximum instantaneous concentration of hydrocarbons emitted. This is the converse of the effect on total mass of hydrocarbons emitted, and may be thought to be contrary to normal incinerator practice. The upper portion of Figure 7 indicates that, at lower kiln temperatures, high peak heights can occur under high charge surface area conditions, even though the charge mass is low, which again, is in contrast to the peak area results. At higher kiln temperatures (1366 K, 2000°F) the effect of charge surface area alone is much less significant.

It should be noted, however, that the results gathered from the peak height data are much less precise than those from the peak area data. Peak heights varied to a much greater extent as compared to peak area data from replicate tests, especially at very high kiln temperatures. This fact is evident from the variability accounted for by each model, and may account for the somewhat counterintuitive results seen in Figure 7 for high kiln temperatures (1366 K, 2000°F). These curves indicate slight decreases in peak intensities with increasing charge surface area at constant charge mass. Even with this in mind, the results presented in Figure 7 still show the effect of increasing peak intensity with increasing kiln temperature and the qualitative results that peak area and peak intensities are quite different phenomena.

Contour plots for the other wastes were somewhat different. The HDPE showed a very steep surface area dependence especially at very low charge mass values. PS and PVC also showed strong surface area effects, but the role of kiln temperature was more ambiguous. Note that for the PVC waste, peak heights were very much smaller and peak durations much longer than those for the LDPE waste at similar test conditions (Figure 5).

Physical Interpretation of Results

It is likely that the formation of puffs is governed by a number of related chemical and physical processes. High kiln temperatures enhance rapid devolatilization of the solids, thus increasing the rate of formation of volatile gases to consume and displace the excess flue gas oxygen from the main burner. This may explain the (unexpected) significant effect of kiln temperature on the maximum instantaneous concentration of hydrocarbons in the puff (peak height). However, it is interesting to note that, in all cases, increasing kiln temperature decreased the total mass of hydrocarbons emitted (peak area). This points to the beneficial (and not unexpected) effects of high temperatures to enhance oxidation mechanisms. Clearly, definition of an optimum condition is nontrivial. In practice, afterburners must be able to handle large instantaneous pulses of wastes from the kiln, and so the results on peak height are of practical significance.

That surface area appears to be an important parameter, under several conditions, indicates the importance of physical processes such as heat transfer to the solid and devolatilization from the surface. Decreasing surface area of the solid usually decreases both the intensity of the puff and the total hydrocarbon mass emitted. The exceptions to this occurred at high kiln temperatures when heat transfer and subsequent devolatilization are both more rapid.

Heat transfer is clearly not always the dominant mechanism, since there were vast differences in behavior between waste types with similar heat transfer properties. Some of this is due to differences in physical transformations of the solid rods upon landing on the hot refractory surfaces. Some plas-

tics, especially at higher kiln temperatures, quickly melted and formed a pool, the surface area of which then had little to do with the initial surface area of the solid. Stoichiometry is also another important consideration. The different wastes require different amounts of oxygen for combustion. A given mass of PVC requires only 40 percent of the oxygen that the same mass of LDPE or HDPE requires. Similarly, the oxygen requirement of PS is 90 percent of that required by LDPE or HDPE.

PVC rods had the slowest rate of volatile release, for all charge surface areas, and therefore always formed the least intense, but longest puffs. Their effluent could be handled best by an afterburner. This was evident from the volatile hydrocarbon traces (Figure 5) and also from thermogravimetric analysis (TGA). These "devolatilization profiles" indicate that while PVC begins to lose mass at a lower temperature as compared to both LDPE and HDPE, the mass loss rate is slower. Programmed at a temperature ramp of 30 K/min (54°F/min) in a nitrogen atmosphere, the PVC begins to lose mass at approximately 525 K (486°F) and is still losing mass at 1175 K (1656°F). Both LDPE and HDPE under the same conditions, begin losing mass rapidly at approximately 675 K (756°F) and essentially all mass is lost by 750 K (891°F). Clearly, volatile release rates are significant in characterizing the propensity of solid wastes to form transient puffs. The polyethylene (PE) wastes had the most rapid rate of volatile release, and thus are most likely to cause difficulties in the downstream afterburner.

Transient Puff Composition

Discussion to this point has focused on measurements of transient puffs composed of volatile hydrocarbons, as sampled by a heated (420 K, 300°F) sample line and analyzed in real-time by a FID. This section is concerned with the following issues: (a) what fraction of these hydrocarbons consisted of methane, (b) what was the probable source of these hydrocarbons, and (c) what hazardous constituents, as defined by RCRA, Appendix VIII,[11] are likely to be present in the puff. It should be emphasized that these are in no way indicative of what can escape from a rotary kiln incinerator system. Rather, they provide an indication of what can be formed in the rotary kiln and therefore what must be destroyed in the afterburner downstream.

Table III. Preliminary overcharging experiment.

Main burner (high fire)		
Natural gas, m^3/h (cfh)	10.2	(360)
Air, m^3/h (cfh)	109.0	(3850)
Excess air, %	10	
Kiln temperature, K (°F)	1644	(2500)
Empty polyethylene bottles (1-gal), g	496	
Three charges at 5-min intervals		
Total sampling time (glass SASS), min	16	
Total volume of stack gas, m^3/16 min	31.79	
Volume sampled, m^3	0.58	
Particle (solids) loading		
Filter, mg	898	
Probe rinse, mg	571	
Total, mg/0.58 m^3	1469	
Concentration, mg/m^3	2533	
Extractable organics (TCO and GRAV results from glass SASS samples)		
Filter and probe rinse, mg	8.247	
XAD-2 resin, mg	10.430	
XAD-2 resin condensate, mg	0.189	
Water impingers, mg	1.238	
Total, mg/0.58 m^3	20.104	
Concentration, mg/m^3	34.662	
Compounds identified from XAD-2 resin		
Toluene		
Trimethylcyclopentane		
Phenylacetylene		
Styrene		
Propynylbenzene		
Naphthalene		
Methylnaphthalene		
Acenaphthalene		
Fluorene		
Anthracene or phenanthyrene		
Methylenephenanthyrene		
Fluoranthene or pyrene		
Acepyrene		
Acefluoranthene		

Methane

Of concern was that the hydrocarbons measured might consist primarily of methane, and that this may be derived from unburned gaseous fuel, rather than from the solid waste. Comparison of total hydrocarbons and methane showed that: (a) methane comprises between 10 and 20 percent of the total volatile hydrocarbons, and (b) the proportion of methane to this total is constant over the duration of the peak. Puffs were also analyzed under special conditions when the main burner gas (and a proportional amount of air) was turned off, but the refractory was still sufficiently hot to maintain appropriate kiln temperatures. The proportion of methane increased slightly to 20–30 percent. Clearly, methane did not originate from the main flame, which was off. Therefore, the evidence strongly suggests that the entire transient hydrocarbon trace, used as the response in the previous section, originated from the waste solid, not from the quenching of the primary flame.

Hazardous Constituents

More detailed compositions of the transient puffs were measured using stack sampling and VOST and SASS trains,[8,9] in conjunction with GC/MS analysis.[12] We first conducted screening experiments to determine what was contained in the total of three puffs resulting from three separate empty 1-gal polyethylene bottles charged at 5-minute intervals, crudely simulating a practical charge rate of 12 charges per hour, but with the afterburner off. Kiln operating conditions and results are shown in Table III. Note that the total extractable organics constitute less than 1 percent of the total particulate loadings, as determined from the SASS filter and probe rinse. This was at a deliberate failure mode condition of only 10 percent excess air (SR = 1.1) but at a high kiln temperature of approximately 1644 K (2500°F). Table

III also lists compounds identified from a chromatogram of the XAD-2 resin extract. This segment of the SASS train yields information on semivolatile organic compounds ranging from C_7 through C_{20}. Many PICs were identified, even from this very restricted sample. Note, however, that subsequent data indicated that naphthalene could be formed by the gas flame alone. Clearly, however, a puff entering the afterburner can contain a large variety of compounds originating from incineration of even simple objects like a polyethylene milk jug.

tractable samples from all parts of the SASS train were combined. Results are shown on Table IV. From a selected list of 170 semivolatile Appendix VIII compounds,[11] three POHC/PIC compounds were detected from the baseline test (a), four from the PE test (b), nine in the first PE/PVC test (c-1), seven in the second test (c-2), and four in the PVC test (d). A most significant result is that hexachlorobenzene, 1,2,4-trichlorobenzene, and pentachlorophenol were detected in both PE/PVC tests but *not* in the tests with PVC alone. This is consistent with the transient results described in the preceding section. PVC alone is devolatilized slowly and forms small puffs of low intensity and magnitude. Excess oxygen is not totally depleted or displaced, and even though large quantities of chlorine are available, few chlorinated PICs are formed. PE alone, on the other hand, forms intense puffs of great magnitude. Excess oxygen is nearly totally depleted or displaced, and although no chlorine is present to allow the formation of chlorinated PICs, there is a propensity to form large quantities of soot. Therefore, it is not surprising that the greatest likelihood of chlorinated hazardous compounds being in the puffs occurs when PE and PVC are mixed. The PVC provides the necessary chlorine, and the PE provides the oxygen starved conditions which promote PIC formation. It is also interesting to note that increased aromatic chlorination correlates with transient puff severity (with chlorine present); i.e., is greatest for the PE/PVC tests. Fluoranthene, a polycyclic aromatic hydrocarbon (PAH), on the other hand is formed only under the most severe puff condition (i.e., with PE alone).

The test samples were also analyzed for specific polychlorinated paradibenzo dioxins (PCDDs) and polychlorinated paradibenzo furans (PCDFs). GC/MS with selected ion monitoring was employed on concentrated samples. No PCDDs or PCDFs were detected from the baseline test (a), the PE burn (b), or the solvent blank. The first PE/PVC test (c-1) may contain pentachloro through octachloro dioxins and furans. The second PE/PVC sample (c-2) had many interference peaks in the chromatogram, and no conclusions could be drawn from that sample. The PVC burn sample test (d) may contain pentachloro through octachloro dioxins and furans. These results may be significant in delineating possible routes for forming these species from chlorinated plastics. However, it must be reemphasized that all these samples were drawn during a series of puffs from the kiln exit, prior to the afterburner, and therefore may represent only what must be destroyed by the afterburner or removed downstream. They probably bear no relationship, whatsoever, to emissions at the exit of a practical rotary kiln/afterburner system.

Table IV. Selected RCRA Appendix VIII compounds identified in test burns charging polyethylene and polyvinyl chloride pipe.[a]

	Solvent blank	Baseline[b] (a)	PE (b)	PE/PVC[c] (c-1)	PE/PVC[c] (c-2)	PVC (d)
(2-Ethylhexyl)phthalate		X	X	X	X	X
Naphthalene		X	X	X	X	X
Dichlorobenzene				X	X	X
1,2,4-Trichlorobenzene				X	X	
Hexachlorobenzene				X	X	
Pentachlorophenol				X	X	
Fluoranthene			X			

[a] In all cases, the kiln was at high fire conditions (1339 K, 1950°F), 100 percent excess air (SR = 2.0), 1 rpm kiln rotation, and 9 to 10 charges averaging 270 g (0.595 lb) each, were charged 1 every 10 minutes.
[b] Baseline test sampled auxiliary fuel combustion gas products; no waste material charged.
[c] PE/PVC mixed charges were 50 percent each by weight.

We then explored the potential to produce hazardous compounds as defined by RCRA, Appendix VIII,[11] from simple polyethylene (PE) and polyvinyl chloride (PVC) pipe pieces. Results are presented for a solvent blank and for test conditions:

(a) A baseline in which the exact procedure for charging was followed, but no charge was entered (i.e., the gate was opened and closed).
(b) One test involving PE pipe with nine charges totalling 2.3 kg.
(c) Two separate (replicate) tests involving 50 percent PE and 50 percent PVC (PE/PVC) pipe, each test consisting of 10 charges totalling 2.7 kg.
(d) One test involving 10 charges of PVC pipe totaling 2.9 kg.

In all cases, the kiln was at high fire conditions (1339 K, 1950°F) and 100 percent excess air (SR = 2.0), and the charges were introduced at a rate of one every 10 mixtures.

Both VOST and SASS sample trains were utilized. The VOST results indicate the presence of benzene in all of the tests including the baseline and ethylmethylbenzene and trichloroethane from the PE/PVC tests. Extractable samples from all parts of the SASS train were combined. Results are shown on Table IV. From a selected list of 170 semivolatile Appendix VIII compounds,[11] three POHC/PIC compounds were detected from the baseline test (a), four from the PE test (b), nine in the first PE/PVC test (c-1), seven in the second test (c-2), and four in the PVC test (d). A most significant result is that hexachlorobenzene, 1,2,4-trichlorobenzene, and pentachlorophenol were detected in both PE/PVC tests but *not* in the tests with PVC alone. This is consistent with the transient results described in the preceding section. PVC alone is devolatilized slowly and forms small puffs of low intensity and magnitude. Excess oxygen is not totally depleted or displaced, and even though large quantities of chlorine are available, few chlorinated PICs are formed. PE alone, on the other hand, forms intense puffs of great magnitude. Excess oxygen is nearly totally depleted or displaced, and although no chlorine is present to allow the formation of chlorinated PICs, there is a propensity to form large quantities of soot. Therefore, it is not surprising that the greatest likelihood of chlorinated hazardous compounds being in the puffs occurs when PE and PVC are mixed. The PVC provides the necessary chlorine, and the PE provides the oxygen starved conditions which promote PIC formation. It is also interesting to note that increased aromatic chlorination correlates with transient puff severity (with chlorine present); i.e., is greatest for the PE/PVC tests. Fluoranthene, a polycyclic aromatic hydrocarbon (PAH), on the other hand is formed only under the most severe puff condition (i.e., with PE alone).

The test samples were also analyzed for specific polychlorinated paradibenzo dioxins (PCDDs) and polychlorinated paradibenzo furans (PCDFs). GC/MS with selected ion monitoring was employed on concentrated samples. No PCDDs or PCDFs were detected from the baseline test (a), the PE burn (b), or the solvent blank. The first PE/PVC test (c-1) may contain pentachloro through octachloro dioxins and furans. The second PE/PVC sample (c-2) had many interference peaks in the chromatogram, and no conclusions could be drawn from that sample. The PVC burn sample test (d) may contain pentachloro through octachloro dioxins and furans. These results may be significant in delineating possible routes for forming these species from chlorinated plastics. However, it must be reemphasized that all these samples were drawn during a series of puffs from the kiln exit, prior to the afterburner, and therefore may represent only what must be destroyed by the afterburner or removed downstream. They probably bear no relationship, whatsoever, to emissions at the exit of a practical rotary kiln/afterburner system.

The main conclusions to be drawn from this section are: (a) that transient puffs originating from the overcharging of rotary kilns can comprise several harmful organic compounds, and (b) that mixtures of two solid plastic wastes can lead to formation of hazardous constituents that are not formed from either one alone.

Conclusions

A laboratory-scale rotary kiln simulator can provide useful insight into the complex phenomena that control the magnitude of transient puffs from the incineration of plastic surrogate

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.

wastes. These transient puffs can be important, and they are very easily generated even at high excess air values. With respect to solid plastic wastes, increasing kiln temperature does not necessarily decrease the instantaneous intensity of the puff and may in fact cause an increase, due to the accelerated solid devolatilization rate. However, the total integrated mass of hydrocarbons exiting the kiln is decreased by increasing kiln temperature. Both instantaneous intensity and integrated mass of the puff are strong functions of both the mass of the waste charge and its surface area as well as its solid waste composition. It is desirable to minimize the surface to volume ratio for solid wastes introduced into the kiln in a batch mode in order to minimize the occurrence of puffs.

The transient composition of the effluent leaving the kiln during the batch incineration of simple prototype plastic wastes can consist of many hazardous compounds. Mixtures of plastics can lead to more hazardous constituents than result from a single plastic incinerated alone. This synergism can be interpreted in the light of physical phenomena during batch incineration. Results suggest that, in a practical kiln incinerator system, the role and proper design of the afterburner is critical, and must be able to handle these transient conditions.

The data suggest that transient puffs originate through a complex mix of chemical and physical processes in which heat transfer to the solid waste, the rate of devolatilization and stoichiometry are important. These processes are strongly dependent on the nature of the solid waste, how it deforms and melts prior to devolatilization, and how the products contact the oxygen in the main flue gas. Future work could include quantifying the waste characteristics leading to transient puffs. Current results suggest that waste characterization through the use of thermogravimetric analyses may be useful.

Acknowledgments

The authors would like to thank EPA's Bill Lowans, Ray Grote, Nelson Butts, and Richard Perry for their technical advice and assistance in the construction and data collection phases of this project. The help of the Technical Support Office of EPA's Air and Energy Engineering Research Laboratory (AEERL), in the coordination of the collection and analysis of the VOST and SASS samples is also gratefully acknowledged. Special thanks to Bob Hall, Branch Chief, Combustion Research Branch, AEERL, for his guidance and support. We would also like to thank the U.S. EPA Hazardous Waste Engineering Research Laboratory (HWERL) for partial support of this work.

Disclaimer

The research described in this article has been reviewed by the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

References

1. I. Frankel, N. Sanders, G. Vogel, "Survey of the incinerator manufacturing industry," *Chem. Eng. Prog.* **3**: 44 (1983).
2. C. Brunner, "Design of Sewage Sludge Incineration Systems," in *Pollution Technology Review Series No. 71*, Noyes Press, Ridge Park, NJ, 1981.
3. H. W. Fabian, P. Reher, M. Schoen, "How Bayer incinerates wastes," *Hydrocarbon Process.* **4**: 183 (1979).
4. R. K. Tanner, "Incineration of industrial waste," *Prog. Energy Combust. Sci.* **5**: 245 (1979).
5. T. A. Bonner, C. L. Cornett, B. O. Desai, J. M. Fullenkamp, T. W. Hughes, M. L. Johnson, E. D. Kennedy, R. J. McCormick, J. A. Peters, D. L. Zanders, "Engineering Handbook for Hazardous Waste Incineration," Monsanto Research Corp., EPA-SW-889 (NTIS PB 81-248 163), U.S. EPA, Industrial Environmental Research Laboratory, Cincinnati, OH, 1981.
6. A. Trenholm, P. Gorman, G. Jungclaus, "Performance Evaluation of Full-Scale Hazardous Waste Incinerators—Volumes I–V," Midwest Research Institute, EPA-600/2-84-181e (NTIS PB 85-129 542), U.S. EPA, Industrial Environmental Research Laboratory, Cincinnati, OH, 1984.
7. R. W. Ross, F. C. Whitmore, R. A. Carnes, "Evaluation of the USEPA CRF incinerator as determined by hexachlorobenzene incineration," *Haz. Waste* **1**: 581 (1984).
8. L. D. Johnson, R. G. Merrill, "Stack sampling for organic emissions," *Toxicol. Environ. Chem.* **6**: 109 (1983).
9. L. D. Johnson, "Detecting waste combustion emissions," *Environ. Sci. Technol.* **20**: 223 (1986).
10. C. R. Hicks, *Fundamental Concepts in the Design of Experiments*, 2nd edition, Holt, Rinehart and Winston Inc., New York, NY, 1973.
11. Resource Conservation and Recovery Act, Subtitle C, Sections 3001-3013, 42 N.S.C., Sections 6921-6934 (1976) and Supplement IV (1980).
12. R. H. James, R. E. Adams, J. M. Finkel, H. C. Miller, L. D. Johnson, "Evaluation of analytical methods for the determination of POHC in combustion products," *JAPCA* **35**: 959 (1985).

Dr. Linak is a visiting NAS/NAE postdoctoral fellow with the Air and Energy Engineering Research Laboratory (AEERL), U.S. EPA, Research Triangle Park, NC, 27711. Mr. Kilgroe and Mr. McSorley are project officers with AEERL. Dr. Wendt is a NAS/NAE senior visiting scientist with AEERL, and a professor of Chemical Engineering at the University of Arizona, Tucson, AZ, 85721. Dr. Dunn is a professor of Mathematical Sciences at the University of Arkansas, Fayetteville, AR, 72701. This work is part of an ongoing EPA in-house research program conducted at the Air and Energy Engineering Research Laboratory, U.S. EPA, Research Triangle Park, NC, 27711 examining the combustion characteristics of hazardous waste incineration.

This manuscript was first submitted for peer review June 2, 1986. The revised manuscript was received November 21, 1986.